THE GOLDEN JUBILEE OF THE CHEMICAL SOCIETY OF JAPAN

The Chemical Society of Japan originates in the "Kwagakukwai" (Chemical Society), the first general meeting of which was held on April 26, 1878, at the Professors' Common Room of the University of Tokyo. Soon after the Restoration of 1868, modern sciences were introduced into this country, and in 1873, several courses of special education were established in Tokyo Kaisei Gakko (Tokyo Enlightenment School), the forerunner of the University of Tokyo and a college of an American model. In 1877, Tokyo Kaisei Gakko was reorganized to the University of Tokyo, and graduates were admitted to their degrees for the first time in that year. In the next year, the graduates and students of the Chemistry Course of the Department of Science of this University organized the Chemical Society referred to above. The first President was the late Dr. Mitsuru Kuhara, a graduate of 1877, and later Professor of Organic Chemistry and sometime President of the Imperial University of Kyoto. The word Tokyo was added to the name of the Society soon after, and it was changed to Japan since 1921, to make the name fit for wider scope of the activity of the Society.

As the papers communicated to the Society at its first meeting the following are recorded: viz., "An idea of sanitary chemistry and the necessity of its progress in Japan" by M. Kuhara, and "On Graebe's remarkable achievement regarding artificial alizarine" by E. Watanabe. First of these two was continued at the second meeting held on May 17, when another paper, "The manufacture of Japanese paper" by S. Imai, was also read. On looking upon these subjects we can imagine how eager were those who established this Society to try to do some researches in those early days when exact sciences were just introduced into this country, and laboratory equipments were very meagre. Unhappily the Society not having its publications on those days, the text of these papers cannot be approached now.

The first number of the publications of the Tokyo Chemical Society appeared in February 1880, as the Vol. I, No. 1 of the "Tokyo Kwagakukwaishi" (Journal of the Tokyo Chemical Society). The Journal was quarterly until 1887, and during 1888–1903 ten numbers were published every year. Since 1904 it is monthly. In 1921, the name of the Journal was changed to "Nippon Kwagakukwaishi" (Journal of the Chemical Society of Japan), as the name of the Society was so changed. From the beginning this Journal has been published in Japanese language, and contains original papers communicated to the Society, abstracts of chemical

papers published in other journals, miscellaneous notes, proceedings of the Society, etc. In 1926, another publication "Bulletin of the Chemical Society of Japan" was launched. This Bulletin is printed in English, French or German language and contains the papers communicated to the Society, original or translation of those in Japanese, as well as abstracts of papers published in Japan.

Another publication of the Society is "Kwagaku Yakugoshu" (English-Japanese Dictionary of Chemical Terms) published in 1891. It was out of print for a long time. Meanwhile, Professors Takamatsu and Sakurai, with their friends, compiled and published "Kwagaku Goi" (A Vocaburary of Chemical Terms) in 1900, the second and third editions of which apeared in 1906 and 1918 respectively, with revisions and additions each time. Now in commemoration of the jubilee of this Society, the enterprise was again taken up by the Society, the authors of the latter work having presented its copyright to the Society. New edition of the Vocaburary will be issued in a near future, and French will be added also to English, German and Japanese in its present edition.

The Chemical Society of Japan administers three special funds besides its general fund: viz., Sakurai Fund, Ikeda Fund and Osaka Fund. The Sakurai Fund was donated to the Tokyo Chemical Society in 1908 by the friends and pupils of Professor Joji Sakurai, now President of the Imperial Academy and of the National Research Council of Japan and Emeritus Professor of the Imperial University of Tokyo, to commemorate his completion of twenty-five years as Professor of Chemistry in that University. The income of this fund is to be used in awarding the Sakurai Medal with an honorarium to the author of meritorious papers in the Society's Journal or any other publications. The first recipient of this Medal in 1910 was Prof. M. Ogawa, now President of the Tohoku Imperial University at Sendai, and the second in 1911, Prof. U. Suzuki, now Dean of the Faculty of Agriculture in the Imperial University of Tokyo. The Ikeda Fund is a fund contributed by the friends and pupils of Professor Kikunae Ikeda in 1925, to commemorate his sixtieth birthday and his service as the Professor of Physical Chemistry in the Imperial University of Tokyo. The income of this fund is to be used for assisting scientific publications, and the fund itself may be expended if necessary. The Osaka Fund was presented to the Society by Professor Yukichi Osaka in 1927, from the sum contributed by his friends and pupils to commemorate his sixtieth birthday and his service as the Professor of Physical Chemistry in the Imperial University of Kyoto, another part of this sum having been devoted to assist the publication of "Sexagint," a collection of papers dedicated to him by his pupils on that occasion. The income of this fund as well as the fund itself may be

expended for the promotion of chemistry by any method the Council of the Society decides fit.

In the domain of the international relations following points may be enumerated. First, when the International Committee on Atomic Weights was formed in 1899, Tokyo Chemical Society nominated Professors Sakurai and Ikeda as its representatives. In this point, perhaps it may be added that they addressed an open letter (*Chem. News*, **89** (1904), 305) to Prof. F. W. Clarke, Chairman of the Sub-Committee, criticising the policy of adopting both oxygen and hydrogen standards, and whether in consequence of this letter or not, the oxygen standard has since become the only official standard of International Atomic Weights. The second is the nomination of Professor Osaka as a member of the International Committee for the publication of "Annual Tables of Constants and Numerical Data: Physical, Chemical and Technological." This Committee is an outcome of a resolution passed at the Seventh International Congress of Applied Chemistry, held in London, 1909, and Tokyo Chemical Society, in conjunction with Tokyo Physico-Mathematical Society, Society of Chemical Industry and Agricultural Society, elected Professor Osaka as the Japanese member of the International Committee, and tried to collect necessary data and send them to the General Secretary at Paris, as well as making some donations. The third is the joining to the International Association of Chemical Societies. This Association was formed in 1911, and consisted of one representative Society from each country, and Tokyo Chemical Society joined it in 1912. Perhaps it may be added that all these three were since absorbed in the International Union of Pure and Applied Chemistry, formed together with the International Research Council in 1919. The International Association of Chemical Societies was declared dissolved at the first Conference of the International Union of Pure and Applied Chemistry, held in Rome, 1920. The publication of the Annual Tables of Physico-Chemical Constants and Numerical Data was annexed to the Union at the same meeting, but Professor Osaka is still working as a member of the International Committee for its Publication. The International Committee on Atomic Weights was also affiliated to the Union at that meeting, and was reorganized to the International Committee on Chemical Elements in 1921. The representation of Japan in the International Research Council and the affiliated Unions is assumed by the National Research Council, established as a Government institution in 1921, and although this Council is now working as a self-governing and self-co-opting body, on its first formation the Chemical Society of Japan nominated two members of the National Research Council as its representatives in the persons of Professors Ikeda and Suzuki.

As mentioned in the beginning of this short note, the Chemical Society of Japan is an out-growth of the "Chemical Society" established in 1878, and just completes fifty years of its existence. The number of its original members was 24, while its present strength is 1407 (2 Honorary Members, 710 Fellows and 695 Associates). Of the 24 original members, we can happily count six among our present Fellows: viz., Prof. T. Takamatsu, this year's President of the Society, and Drs. Y. Hiraga, T. Ishido, Y. Koga, I. Nakazawa and H. Yoshida. Hearty congratulations of the Society must be offered to them!

Koichi MATSUBARA.

Addendum. The minutes of the Twenty-fifth Anniversary Meeting of the Tokyo Chemical Society, held on May 9, 1903, appears in *Chemical News*, **87** (1903), 310. The Eighth Annual Meeting, held on April 10, 1886, is also reported in the same journal (*Chem. News*, **53** (1886), 284). Papers read before the Chemical Society of Japan at the monthly and annual meetings since January of 1927 are noticed in the Bulletin of the Society, Vol. II, No. 5, and the following parts.

THE PRECIPITATION OF THE GOLD AND THE SILVER FROM THEIR DILUTE SOLUTIONS.

By **Mataichi YASUDA.**

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It is well known that the precious metals precipitate from their solutions by contact with the base metals. It is also known that the metallic couples such as zinc-copper, zinc-lead and others were studied as reducing agents[1] and lead-aluminium couple was used to precipitate gold for analytical purposes.[2] It seems probable that the higher electric potential difference between the metals is more favourable to precipitate the precious metals from their exceedingly dilute solutions such as sea water. As was described in the former paper[3], I believe that the gold and the silver in sea water exist in ionic states, thus $Au^{\cdots}$, $Au^{\cdot}$ and $Ag^{\cdot}$. The metallic couples, therefore, may apply to precipitate the precious metals in this case.

The fact that the precious metals exist in sea water was known very early times, and since then many works were published on this subject.[4]

Since two years I have studied the chemical properties of metallic manganese, and found that this metal is suitable to precipitate the precious metals from exceedingly dilute solution such as sea water, because of its close resemblance to the metallic magnesium, and its chemical reactions is much slower in the sea water than the latter.

At first I tried with a couple of manganese and lead. It is, however, very difficult to obtain the couple directly by dipping the metallic manganese in the solution of lead, for the adhered lead on the manganese has spongy appearance and is easily detached therefrom. I, therefore, made an alloy by mixing the manganese and the lead. The purpose of the metallic couple or alloy is to utilize the galvanic current which occurs between these metals, the easily oxidizable metal, the manganese, being anode, and the nobler

(1) J. J. Hood, *J. Soc. Chem. Ind.*, **14** (1895), 808; Christy and Butters, *Chem. News*, **75** (1897), 309; H. Becker, *Chem. Zeit.*, **21** (1897), 296.

(2) *Proc. Chem. Met. a. Min. Soc. South Africa*, Sept. 1913.

(3) M. Yasuda, this journal, **2** (1927), 322.

(4) Malaguti and Durocher, *Compt. rend.*, **49** (1859), 463; Liversidge, *Chem. News*, **74** (1896), 146; A. Münster, *J. Soc. Chem. Ind.*, **11** (1892), 351; Liversidge, *Proc. Roy. Soc. New South Wales*, **29** (1895), 335; Liversidge, *J. Chem. Soc.*, **71** (1897), 298; J. R. Don, *Tran. Am. Inst. Min. Eng.*, **27** (1897), 615; L. Wagoner, *Trans. Am. Inst. Min. Eng*, **31** (1901), 807; F. Haber, *Z. angew. Chem.*, **40** (1927), 303; J. W. Pack, *Min. and Sci. Press*, **77** (1898), 154; P. de Wilde, *Arch. Sci. phys. Nat.*, 4th ser. **19**. 559; A. Wiesler, *Z. angew. Chem.*, **19** (1906), 1795; H. Koch, *Kolloid Z.*, **22** (1918), 1.

metal, the lead, cathode. The galvanic current will continue until the anode is oxidized and is covered by the film of mangano-manganese oxide. By this galvanic current the precious metals in sea water will deposit on the cathode metal, lead.

As above stated, the gold which is able to effect the galvanic current is the ions, $Au^{\cdots}$ and $Au^{\cdot}$. The chlorine ion oxidizes the manganese and the gold deposited on the lead. The silver will behave the same as the gold. The manganese can changes its valency in several stages, and form many oxides, some of which are soluble and others insoluble as was described by Spring and be Boeck[1]. If we put the manganese-lead couple into the sea water, no perceptible change in the solution was found at begining, but after some hours the soluble hydroxide is oxidized, and hydrated black mangano-manganic oxide adhered on all parts of the vessel.

It may be also supposed as J. M. Stuart and G. D. Bengough[2] stated, the manganese hydroxide which is formed from the manganese charged positively in colloidal state and neutralized the ion $AuCl_4'$ and changes to single salt $AuCl_3$ or AuCl, and the metallic ions $Au^{\cdots}$ or $Au^{\cdot}$ neutralized again with negatively charged metal and is deposited on the lead. Here the passivity of the metallic manganese which is known to be very unstable, and soon recover its electric potential and the reactions go on.[3] In general it is recognized that the metal resemble to zinc or magnesium in its behaviors.

At first, I have carried out the experiments on several couples of metals, such as copper-manganese, manganese-lead and lead-aluminium. The preparation of the alloys of lead and aluminium[4] or lead and manganese[5] are very difficult, but the mechanical or heterogeneous mixtures of lead and aluminium or lead and manganese can easily be prepared. The experiment on lead-manganese couple was carried out in the following manner.

The powdered lead and manganese are put together in a steel case and are strongly hammered with an air hammer as hard as possible, and at last a thin plate of 0.07 mm. thickness was obtained. The plate thus made was then cut into rectangular sheet and hang into a beaker in which two or three litres of sea water being contained, and stir the water with a appropriate stirrer. After some hours, the plate is taken out and rolled to a small volume and put in a crucible. Then 2 or 3 grammes of lead oxide are added and heated to a fused state to oxidise the remaining manganese in the alloy,

(1) Spring and de Boeck, *Bull. soc. chim.*, [2] **48** (1887), 170.
(2) J. M. Stuart and G. D. Bengough, *Chem. News*, **161** (1922).
(3) H. Küssner, *Z. Elektrochem.*, **16** (1910), 758.
(4) A. G. C. Gwyer, *Z. anorg. Chem.*, **57** (1908), 149.
(5) R. S. Williams, *Z. anorg. Chem.*, **55** (1907), 91.

and obtained a button and cupelled. The gold or the silver-gold bead thus obtained is weighed, and then dissolved in nitric acid (specific gravity, 1.18), and the remaining gold is washed with water, dried, heated and weighed as usual manner. It was confirmed that the initial lead-manganese couple contains no silver or gold by cupellation four times.

To test the accuracy of the method, artificially made sea waters were used, which contained some sodium chloride, potassium chloride, magnesium sulphate and potassium sulphate as well as known quantities of gold chloride. The results are given in the following table.

TABLE 1.

Solution	Gold added gr./l.	Temp.	% of Mn in alloy	Surface of alloy sq. cm.	Wt. of alloy gr.	Duration of exp. hr.	Gold obt. gr.	% of gold obt.	Gold calc. for 1000 kg. alloy gr.
Aq. sol.	2.7×10^{-4}	15°	2	18.00	1.3749	5	1.15×10^{-4}	19.7	81.7
Aq. sol.	„	28°	2	17.96	1.4087	28	0.65 „	11.6	42.2
Sal. wat.	„	18.5°	„	53.90	4.2940	69	3. „	53.8	64.3
Sal. wat.	3×10^{-4}	18.5°	„	27.72	1.4824	69	3. „	50.0	20.2

The volume of solution used in the experiment = 2 litres.
Aq. sol. = aqueous solution.
Sal. wat. = saline water.

Next, the natural sea water was tested which had been obtained at a point four miles off the coast of Kominato Bay, south eastern sea from Tokyo. The results are as follows.

TABLE 2.

% of Mn in alloy	Surface of alloy sq. cm.	Wt. of alloy gr.	Total duration of exp. hr.	Gold-silver bead obt. gr.	Gold obt. gr.	Gold calc. for 1000 kg. alloy gr.
8%	28.50	2.0284	641	27×10^{-6}	0.68×10^{-6}	3.4
8%	28.42	2.1000	641	77×10^{-6}	——	——
9.05%	34.40	4.9255	467	85.5×10^{-6}	——	——

Three litres of sea water was used each time, and after some hours it was thrown away and fresh sample of three litres of sea water was introduced into the vessel, and so on. By this manner the water was changed six times in each experiment, so in total eighteen litres of sea water was used. The weight of the bead, therfore, was obtained from 18 litres of the sea water.

Next, some excess gold was added to the Kominato Bay sea water and the gold content was raised to 37 mg. per one cubic meter, and the experiments were done using couples of various contents of manganese. The results are as follows.

TABLE 3.

% of Mn in alloy.	Thickness of alloy mm.	Surface of alloy sq. cm.	Weight of alloy		Wt. of Au-Ag bead gr.	Wt. of gold gr.	Gold adhered on 1 sq. cm. of alloy gr.
			Before exp. gr.	After exp. gr.			
1	0.193	24.38	1.3384	1.3280	10×10^{-6}	——	——
2	0.100	20.30	2.0307	1.9994	10.7 "	3.4×10^{-6}	0.17×10^{-6}
2	0.100	40.80	2.1191	——	16.5 "	6.6 "	0.16 "
3	0.075	36.40	1.5621	1.4984	31.7 "	9. "	0.27 "
4	0.113	26.40	1.6998	1.7109	390. "	18. "	0.68 "
4	0.156	30.32	2.7317	2.7552	770. "	30. "	0.97 "
4	0.130	99.76	7.5199	7.5656	113. "	43. "	0.43 "
5	0.060	46.00	1.6604	1.6649	80. "	15. "	0.32 "
6	0.096	42.78	1.8518	1.8396	34.2 "	10. "	0.25 "

The durations of these experiments were 100 hours, the temperatures, 10–20° C., and the volumes of the sea water, three litres. From these experiments it seems that the 4% alloy gives best result. The weight of alloy decrease in some cases, for the manganese oxidized and removed as oxide or hydroxide from the plate. I have collected the precipitate settled down to the bottom of the vessel, and obtained two samples, about 0.5 gr. in each case, and wrapped with a lead foil and heated with lead oxide in a crucible, and obtained a button and cupelled. In this way, a bead of gold or silver was not obtained. So it is clear that the gold or silver does not precipitate with the oxide or hydroxide of manganese.

Next, another experiment was done with sea water taken at Atami Bay which contained 3 mg. of gold in a cubic meter. And moreover, the experiments were extended to the waters which were made by adding some gold chloride to the Atami Bay water. The results are as follows:

TABLE 4.

Gold content mg. in cb. meter	Thickness of alloy mm.	Surface of alloy sq. cm.	Weight of alloy		Gold adhered gr.	Gold adhered on 1 sq. cm. gr.	Water
			Before exp. gr.	After exp. gr.			
3	0.07	37.4	2.6074	2.5232	2.3×10^{-6}	0.06×10^{-6}	Natural sea water
7	0.055	47.32	2.5440	2.5215	5. "	0.1 "	$AuCl_3$ was added
7	0.075	56.40	2.3453	2.3375	5.8 "	0.1 "	"
10.5	0.055	60.52	2.7027	2.6843	38. "	0.6 "	"
10.5	0.075	54.88	3.3650	3.3635	19.6 "	0.35 "	"
17.5	0.055	36.64	2.0430	2.0180	30.7 "	0.85 "	"
17.5	0.075	74.46	4.1990	4.1950	17.5 "	0.32 "	"
22.9	0.055	56.48	2.3032	2.3000	12.3 "	0.22 "	"
22.9	0.075	89.60	5.7268	5.7068	29. "	0.33 "	"
37	——	——	——	——	——	0.69 "	"

In these experiments an alloy of 5% manganese was used. Three litres of the waters were taken, the temperature of which was 23°C., and the duration of each experiment was 122 hours.

Theoretical Considerations. We will assume that an alloy plate is moving in the undisturbed solution containing some gold atom. The number of the gold atoms can be calculated as follows. It is known that 6×10^{23} atoms (Avogadro's number) exist in 179.2 grammes of gold. So the number of gold atoms in the sea water which contains a mg. of gold in one cubic meter is $6\times10^{23}\times a\times10^{-3}/197.2 = 3.07\times10^{18}\times a$. It becomes, therefore, in one cubic centimeter, $3.07\times a\times10^{12}$, and the gold atoms come to one square centimeter, or one side of the cube are,

$$(3.07\times10^{12}\times a)^{\frac{2}{3}} = 1.486\times10^{8}\times a^{\frac{2}{3}}.$$

This is the number of gold atoms sweep over the metallic surface of one square centimeter and adhere on the surface. On the other hand, the weight of the single atom of gold is, $197.2\times1.66\times10^{-24} = 0.33\times10^{-21}$ gr., where 1.66×10^{-24} is the weight of one atom of hydrogen. So the weight of gold sweep over the unit area of alloy surface is

$$0.33\times10^{-21}\times1.486\times10^{8}\times a^{\frac{2}{3}} = 0.49\times a^{\frac{2}{3}}\times10^{-13}\,\text{gr.}$$

If we suppose that the sea water contains 32 mg. gold in one cubic meter, or $a = 32$, then the above quantity becomes 4.94×10^{-13} gr.

Assume the metallic surface moves in the water with the velocity of n centimeter per second and there precipitated b gr. of gold during h hours, then,

$$b = 4.94\times10^{-13}\times n\times h\times3600\,\text{gr.}$$

Now taking $n = 3$, and $h = 100$, it becomes,

$$b = 0.54\times10^{-6}\,\text{gr.}$$

This number approximately agrees with the experimental results. In the present experiment the water was stirred constantly with a stirrer, so the concentration of the gold decreases with time. Moreover, the factors such as the free path of ions, hydrodynamic conditions of flowing water on the surface and the influence of temperature must be considered. The above calculations, therfore, by no means an exact one, but only rough approximation.

It is probable that the colloidal gold in the sea water adheres also on the metallic plate for the particles have electric charges.

Summary.

It has been pointed out that the metallic alloy of manganese and lead is suitable to fish the gold from its very dilute solution such as sea water. The method of preparation and the composition of the alloy have been described. The efficiency of its action has been studied.

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APPLICATION OF AN ELECTROMAGNETIC FORCE TO "THERMOBALANCE."

By **Zen-ichi SHIBATA** and **Masaji FUKUSHIMA.**

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Introduction. The "thermobalance" invented by Prof. Honda[1] has wide applications in chemical and metallurgical experiments. But, to our regret, the following defects are met with in its use. (1) By magnifying the sensibility of the balance, the movements on its scale are multiplied even by a small change of weight, and hence it is necessary to interrupt the measurement and change its weight, on the beam of the balance during an experiment. (2) And during this manipulation, the change in the weight of a sample cannot be measured. (3) As the up and down movements of the arms of the balance cause the spring to stretch and contract, the hysteresis of the spring causes an error. (4) The thermocouple cannot be fixed with the sample, so that when the position of the latter is displaced by the change in its weight, it recedes from the former, and the exact reacting temperature is not observable by the thermcouple.

To remedy the above obstacles, the present writers made the following improvements by using an electromagnet.

In our improved apparatus, a current is adjusted in the observing position so that the scale is always set at the zero point. The change in the weight of the sample can be indirectly found from the amount of the current, the sensibility can be magnified, the hysteresis eliminated, and the temperature of the reaction can be found exactly.

Apparatus and Manipulation. The "thermobalance" used in this experiment was that invented by Prof. Honda, and an electromagnet was attached to one side of the beam.

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(1) Honda, *Science Reports of the Tohoku Imperial University*, **4** (1915), 97.

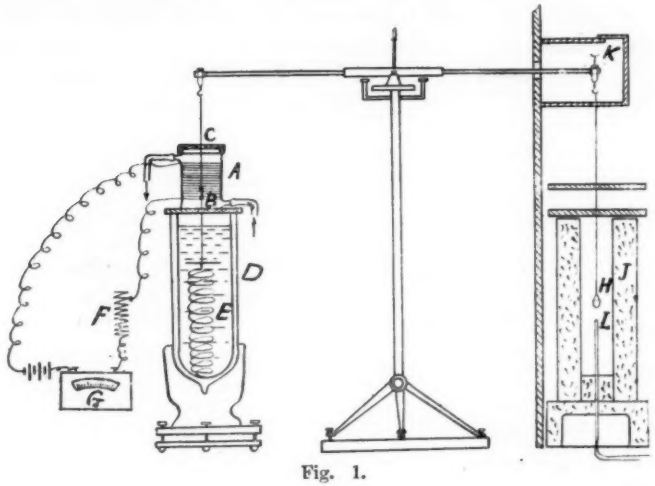

Fig. 1.

Fig. 1 shows the apparatus in which A is a coil wound with silk-wrapped copper wire on a glass cylinder 4.7 cm. in diameter and 6 cm. in length. It is double-walled, and between the walls water is passed to avoid the heating by the current. C is a brass cap and in its centre a small hole is bored, through which passed a slender copper wire. The upper end of the wire is fixed to one arm of the balance and the lower bound to the damper plate, passing through a mild steel rod B, which is 0.4 cm. in diameter and 1.4 cm. in length. Under the plate the upper end of the spring E is fixed. The sensibility of the balance is intensified by using a somewhat weak spring and a less viscous oil, mixed an equal volume of the transformer oil with the petroleum. B is placed downwards from the centre of the coil, to pull it upwards, when the current is passed. The current was lead from a 6 volt battery, and observed with an exact ammeter. The adjustment of the current is easily made by several slide resistances. L is a thermocouple and J a furnace. The parts hatched protect the apparatus from the vibration of the balance by a convection current of air.

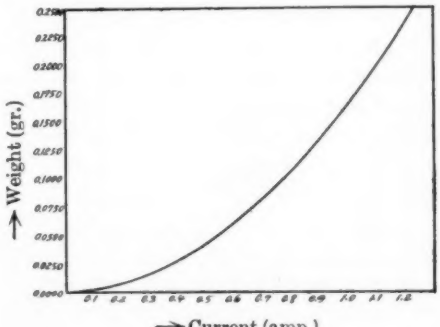

Fig. 2.

In order to obtain the relation between the current and the

weight, 0.3 gr. of the weight is placed on K, and riders on the other side of the arm, to keep the scale at zero, and then on decreasing the weight on K we determine the amount of current sufficient to keep the scale at zero. The results are shown in Table 1 and Fig. 2.

TABLE 1.

Weight gr.	Current amperes	Weight gr.	Current amperes	Weight gr.	Current amperes
0.0000	0.000	0.0700	0.640	0.1600	0.982
0.0010	0.053	0.0750	0.664	0.1650	0.997
0.0020	0.087	0.0800	0.687	0.1700	1.014
0.0030	0.112	0.0850	0.708	0.1750	1.029
0.0050	0.152	0.0900	0.730	0.1800	1.043
0.0080	0.199	0.0950	0.751	0.1850	1.058
0.0100	0.225	0.1000	0.772	0.1900	1.074
0.0150	0.283	0.1050	0.791	0.1950	1.087
0.0200	0.331	0.1100	0.812	0.2000	1.102
0.0250	0.392	0.1150	0.829	0.2050	1.116
0.0300	0.412	0.1200	0.846	0.2100	1.130
0.0350	0.445	0.1250	0.864	0.2150	1.143
0.0400	0.475	0.1300	0.882	0.2200	1.154
0.0450	0.508	0.1350	0.898	0.2250	1.167
0.0500	0.537	0.1400	0.915	0.2300	1.181
0.0550	0.563	0.1450	0.932	0.2350	1.193
0.0600	0.591	0.1500	0.949	0.2400	1.207
0.0650	0.615	0.1550	0.965	0.2450	1.219
—	—	—	—	0.2500	1.232

Results of Experiments. To determine the accuracy of the improved "thermobalance" the present writers determined the decomposition curves of the following five compounds of "Kahlbaum zur analyse."

The thermocouple used was calibrated in the range 300–1200° C. with the Pt-PtRh thermocouple which was certificated at the "Deutsche physikalische-technische Reichsanstalt," and below 300°C. calibrated with the boiling points of water and naphthalene. In the following figures, the ordinates represent the decrease of the weight of the sample, and the abscissa the temperature. The shapes of the decomposition curves are of course somewhat liable to the heating velocity. In the present experiments, it was generally 2 degrees per minute, and at the point where a vigorous decomposition took place 1 degree or less per minute.

Calcium carbonate, $CaCO_3$. The decomposition curve of calcium carbonate is shown in Fig 3 (B). Its decomposition begins at about 400°C., reaches a maximum at 700°C., and finishes at 780°C. to become CaO. The calculated and the observed values of decomposed CO_2 are given below.

$CaCO_3$	CO_2		
	Calculated value	Observed value	Error
0.3175	0.1396	0.1399	+0.0003

Copper sulphate, $CuSO_4 \cdot 5H_2O$. The decomposition curve for the copper sulphate is shown in Fig. 3 (A). The stage of the decomposition is denoted as follows.

$$CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot H_2O \rightarrow CuSO_4 \rightarrow CuO \rightarrow Cu_2O.$$

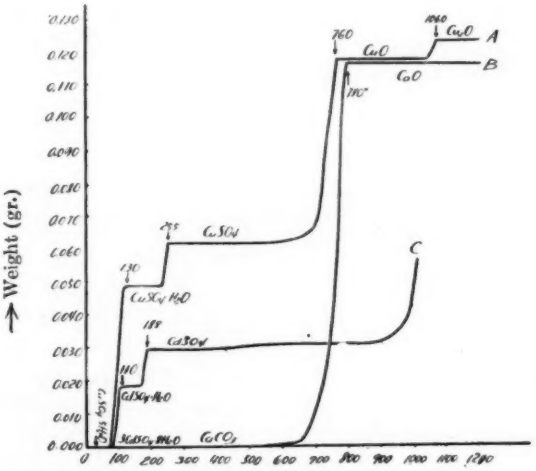

Fig. 3.

The first stage of the reaction occurs at 75–120°C. four molecules of water being removed and one remaining molecule of water escapes at 230–255°C. The anhydrous salt begins to decompose gradually at 600°C. evolving SO_3, and at 760°C. it changes completely to CuO and on further heating it is decomposed to Cu_2O at 1040–1060°C.

The observed data are shown in the following table.

$CuSO_4 \cdot 5H_2O$	$4H_2O$	H_2O	SO_3	$\frac{1}{2}O_2$
0.1723	Calculated value 0.0497	Calculated value 0.0124	Calculated value 0.0553	Calculated value 0.0055
	Observed value 0.0495	Observed value 0.0127	Observed value 0.0556	Observed value 0.0060
	Error −0.0002	Error +0.0003	Error +0.0003	Error +0.0005

Cadmium sulphate, $3CdSO_4 \cdot 8H_2O$. The decomposition curve of this salt is shown in Fig. 3 (C). Cadmium sulphate leaves its crystallising water at two stages, 80–110°C. and 170–190°C. On elevating the temperature, the anhydrous salt begins to decompose at 900°C. The observed data are as follows:—

$3CdSO_4 \cdot 8H_2O$	$5H_2O$			$3H_2O$		
	Calc. val.	Obs. val.	Error	Calc. val.	Obs. val.	Error
0.1614	0.0189	0.0186	+0.0003	0.0113	0.0113	0.0000

Barium chloride, $BaCl_2 \cdot 2H_2O$. The decomposition curve of barium chloride is shown in Fig 4 (D). This salt loses one molecule of water at 70°–100°C. and then its weight begins gradually to decrease above 500°C. The observed data are as follows :—

$BaCl_2.2H_2O$	H_2O			H_2O		
	Calc. val.	Obs. val.	Error	Calc. val.	Obs. val.	Error
0.2581	0.0191	0.0190	−0.0001	0.0191	0.0192	+0.0001

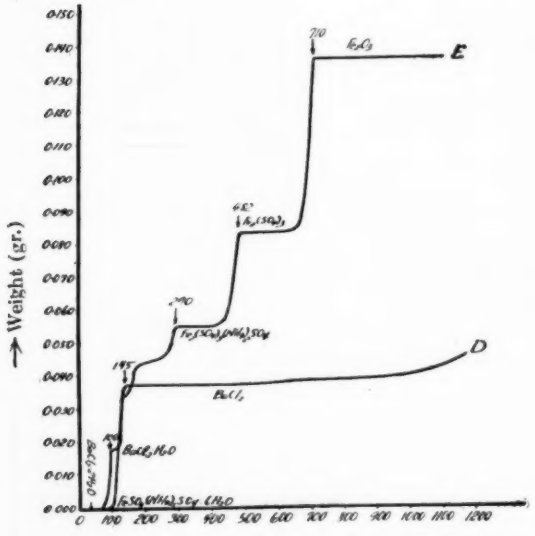

Fig. 4.

Mohr salt, $FeSO_4 (NH_4)_2SO_4.6H_2O$. The decomposition curve of this salt is shown in Fig. 4 (E). The crystallising water is removed at 100°C., one part of ammonia is given off and at the same time is oxidised to ferric salt at 170°C. At 290°C. it becomes $Fe_2(SO_4)_3 (NH_4)_2SO_4$, at 420–490°C. $(NH_4)_2SO_4$ is lost remaining ferric sulphate, and at 650–710° decomposes to ferric oxide. The observed results are as follows :—

$FeSO_4(NH_4)_2 \cdot SO_4 \cdot 6H_2O$	$6H_2O + NH_4$			$(NH_4)_2SO_4$			SO_3		
	Cal.	Obs.	Err.	Cal.	Obs.	Err.	Cal.	Obs.	Err.
0.1700	0.0547	0.0553	+0.0006	0.0286	0.0287	+0.0001	0.0521	0.0528	+0.0007

Summary.

The present writers have applied an electromagnet to the "thermo-balance" to remove the previous defects and succeeded in elevating its sensibility to that of the chemical balance. To determine its accuracy, the decomposition curves of the following five compounds have been determined: calcium carbonate, copper sulphate, cadmium sulphate, barium chloride and Mohr salt.

In conclusion, the authors express their hearty gratitude to Prof. Oishi and Prof. Murakami for their kind directions.

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UEBER NEUE ARBEITEN AUF DEM GEBIETE DER BESTIMMUNG DER STABILITÄT VON RAUCHLOSEM PULVER.

Von **Michael TARLÉ.**

Eingegangen am 7. April 1928. Ausgegeben am 28. Mai 1928.

In der letzteren Zeit sind wieder einige Arbeiten über abgeänderte bezw. neue Untersuchungsmethoden der Stabilität veröffentlicht worden. Das Interesse, welche diese Frage hervorruft, ist leicht verständlich. Die Stabilität—oder chemische Beständigkeit—ist eine Eigenschaft, welche von grosser Bedeutung für das Herstellungsverfahren und für das Lagern des Pulvers ist. Es gibt aber bis jetzt noch keine Untersuchungsmethode dieser Eigenschaft, welche man als einwandsfrei ansehen könnte.

Man kann im allgemeinen die gegenwärtig benutzten Methoden in zwei Hauptklassen teilen; die erste—die qualitative—besteht in der Feststellung der Zeit, welche nötig ist um damit ein Reagenzpapier von den bei Zerlegung des Pulvers auftretenden Gasen gefärbt wird. Die andere Prüfungsart, welche man als quantitativ bezeichnen kann, besteht im Auffangen und in der Bestimmung der Zerfallprodukte während einer Bestimmten Zeit. Zu dieser Klasse gehört auch die Probe, welche u. a. bei dem Amerikanischen Militäramt angewendet wird, und welche in der Bestimmung des Gewichtsverlustes bei einer gewissen Temperatur besteht. Zu derselben Klasse gehört ebenso die Manometrische Probe von Obermüller die Bestimmung des Druckzuwachses, welcher durch die beim Erhitzen des Pulvers auftretenden Gase hervorgerufen wird. Alle diese Proben

leiden an verschiedene Mängel. Zunächst werden sie bei verhältnissmässig hohen Temperaturen vorgenommen, da bei gewöhnlicher Temperatur die Zerfallgeschwindigkeit des Pulvers kleine Werte hat und die Versuche sehr viel Zeit in Anspruch nehmen würden. Das wäre aber aus praktischen Gründen unbequem; ausserdem ist es schwer, bei einen lange dauernden Versuch die Versuchsbedingungen konstant zu halten.

Wenn man, zwecks Reaktionsbeschleunigung, zur Temperaturerhöhung greift, stosst man auf eine neue Schwierigkeit; bei einer hohen Temperatur verdampfen das Lösungsmittel und das im Pulver enthaltene Wasser, die Zerfallreaktion muss also eine andere sein, wie bei normaler Temperatur; die Zusammensetzung der Zerfallprodukte ist auch wahrscheinlich eine andere. Es ist eigentlich unzulässig, auf Grund von Versuchen, welche bei einer hohen Temperatur vorgenommen wurden, auf die Stabilität unter normalen Verhältnissen zu schliessen. Der beste Beweis dafür ist der Umstand, dass die Versuche nach verschiedenen Prüfungsmethoden vorgenommen, oft keine übereinstimmende Resultate liefern. Auch kennt man Fälle, wo ein "stabil" gefundenes Pulver augenscheinlich ohne Ursache plötzlich explodierte... Bei den meisten Untersuchungsverfahren (ausser den Gewichtsverlust- und manometrischen Methoden) werden die entbandenen nitrosen Gase qualitativ entdeckt oder quantitativ bestimmt. Es ist fraglich, ob man in dieser Weise die chemische Beständigkeit und die Zerfallsgeschwindigkeit studieren kann. Die Zersetzungsprodukte bestehen doch nicht nur aus NO_2 und NO, sondern, ausser denselben, aus CO, CO_2, Wasser, Ameisensaüre, Oxalsaüre, Oxybrenztraubensaüre usw.[1] Z. B., in den Seeminen, welche hermethisch geschlossen 7 oder 8 Jahren lagen, hat man folgende Gase gefunden:[2]

O_2	0.3%	H_2	6.5%
CO_2	2.1	N_2O	1.5
CH_4	0.5	N_2	88.9

Man darf also mit Sicherheit annehmen, dass bei verschiedenen Temperaturen die autokatalytische Reaktion verschieden verläuft und dass das Auffangen der nitrose Gasen beim weitem nicht, genügt um in das Wesen dieser Reaktion einen klaren Einblick zu bekommen und um die chemische Beständigkeit mit einiger Sicherheit bestimmen zu können. Es ist bemerkenswert, dass die neueren Arbeiten auf diesem Gebiete sich hauptsächlich mit Gewichtsverlustmethoden beschäftigen. Der Vorteil dieser Methoden besteht in dem Umstande, dass hierbei sämtliche Zerfallprodukte angezeigt werden; zur Messung der Reaktionsgeschwindigkeit eignet sich

(1) Brunswig, " Das Rauchlose Pulver ", 1926, S. 353.
(2) Vieille, Mémorial des Poudres et Salpetres, 15 (1910), 63.

das Verfahren jedenfalls besser, als die übliche Bestimmung eines einzelnen Gases, wie NO_2. Das andere Übel—die hohe Versuchstemperatur—bleibt vorläufig bestehen.

Die Arbeit von v. Meerscheidt-Hüllessem hatte zum Zwecke die Konstruktion eines Apparates, welcher erlaubt hätte das Gewichtsverlust des Pulvers bequem zu beobachten[1]. Die Versuche wurden bei 115°, 8 Stunden täglich vorgenommen und dauerten 8 Tage. Es lassen sich zugleich 37 Muster untersuchen. Der Apparat soll bequem, gefahrlos, ökonomisch und genau arbeiten.

Eine andere vor Kurzem erschienene Abhandlung[2] befasst sich mit derselben Methode und bietet ebenfalls prinzipiell nichts neues an. Die Versuche werden bei etwa 110° vorgenommen und dauern 72 Stunden (9 Tage). Vor dem eigentlichen Versuch werden die Pulvermuster 8 Stunden in offenen Gläsern erhitzt (die Temperatur ist nicht angegeben) um die Reste des Lösungsmittel zu entfernen. Da dabei auch teilweise die Zerfallprodukte entweichen, kann man nicht, streng genommen, die Versuche als quantitativ bezeichnen. Im besten Falle können sie zu Ermittelung der Vergleichswerte dienen.

Zur Messung der Zerfallgeschwindigkeit bei normaler Temperatur (bis etwa 50°), auf die es gerade ankommt, können die bereits besprochenen Methoden nicht angewendet werden. Einen anderen Weg zur Aufklärung dieser Frage versuchen Ryan und Lantz[3] zu finden, indem sie bestrebt sind, den Temperaturkoeffizienten der Zerfallreaktion zu ermitteln. Der Gedanke ist sehr interessant und wird möglicherweise in Zukunft (die Arbeit wird fortgesetzt) fruchtbringend sein; vorläufig scheint es noch bedenklich, die Versuche als eine Stabilitätsprobe "temperature coefficient test" wird sie von den Verfassern genannt) zu betrachten. In einen besonders konstruierten Apparat wurde Luft durch die erhitzten Nitrozelluloseproben durchgeschickt und das von dem Luftstrom während einer bestimmten Zeit mitgenommene Stickstoffdioxyd von einer KI-Lösung wurde absorbiert. Das ausgeschiedene Jod wurde elektrometrisch bestimmt. Die Versuche wurden bei drei Temperaturen—99.5-100°, 116-118° und 136-140—vorgenommen. Die Versuchsdauer beträgt 2 bis 3 Stunden bei der höchsten und etwa 24 Stunden bei der niedrigsten Temperatur. Die lange Versuchsdauer im letzten Falle wird auch die Zeit—20 Stunden—, welche nötig ist, um eine gleichförmige Entwickelungsgeschwindigkeit von NO_2 zu erhalten, verursacht. Für die 100°-Versuche braucht man nur 2 Stunden zu warten. Die Titrationen bei 100°-Versuchen wurden nach 4 Stunden, bei 140° nach 30 Minuten vorgenommen.

(1) *Z. ges. Schiess- Sprengstoffw.*, **21** (1926), 137.
(2) Simon Thomas, *Z. angew. Chem.*, **40** (1927), 991.
(3) *Ind. Eng. Chem.*, **20** (1928), 40.

Man kann diese Methodik nicht als einwandfrei bezeichnen. Der Temperaturbereich (99.5-140°) ist nicht zweckmässig gewählt worden, da zwischen 135° und 140° die Reaktionsgeschwindigkeit-Temperaturkurve einen scharfen Knick aufweist(1), was auf eine plötzliche Änderung des Reaktionsverlaufes hindeutet. In der Tat fand Sapojnikoff, dass die Änderung der Zerfallgeschwindigkeit mit der Temperatur—für eine unlösliche Nitrozellulose mit 13.4% Stickstoff—durch die Formel

$$\frac{V}{t} = A + BT$$

ausgedrückt wird, wo V die Vergrösserung des Volumens der Zerfallgase in der Zeiteinheit t, und T die jeweilige Temperatur bedeutet. A und B sind Konstanten. Zwischen 120° und 135° betragen die respektiven Werte von A und B −2.22 und + 0.0092, zwischen 135° und 150° −64.22 und + 0.48. Wir können also annehmen, dass in der Nähe von 135° eine plötzliche Änderung des Reaktionverlaufes eintritt.

Ryan und Lantz geben keine Definition für-und berechnen nicht den Temperaturkoeffizienten. Wenn wir die Reaktionsbeschleunigung auf Grund der Versuche von Ryan und Lantz nach der Formel

$$\frac{G_1 : G_2}{T_1 - T_2} = K$$

berechnen, wo G_1 und G_2 die Menge von den entwickelten nitrosen Gasen (ausgedrückt in mg. von Stickstoff pro Stunde pro 1 gr. Nitrocellulose) bei den Temperaturen T_1 und T_2 bedeuten, erhalten wir die folgende Werte, (siehe Tafel).

Es fällt auf, dass in einigen Fällen die Grösse K mit der Temperaturerhöhung sinkt; d. h. dass die Reaktion, statt einer Beschleunigung, eine Verlangsamung erleidet. Für eine autokatalytische Reaktion und für bei nahezu gleichen Temperaturbereichen, kann dies nicht stimmen. Vielmehr weist diese Diskrepanz auf einen Fehler der Versuchsmethodik hin. Vor allem müsste bewiesen werden, dass die Menge der entwickelten nitrosen Gase wirklich ein Mass für die Geschwindigkeit der Zerfallreaktion darstellt. Da die Zerfallprodukte aus mehreren anderen Verbindungen bestehen, und da die Zusammensetzung der Zerfallprodukte sich mit der Temperatur ändert, lässt sich auf diesem Wege die Reaktionsgeschwindigkeit kaum, oder nur qualitativ, verfolgen. Andererseits lassen uns die hohe Versuchstemperatur und das Durchsaugen der Luft, welches die Zerfallgase wegnimmt und infolgedessen höchstwahrscheinlich den Reaktionsverlauf ändert, keine bestimmten Schlüsse auf die wirkliche Stabilität des Pulvers ziehen.

(1) Sapojnikoff, *Mem. Poudr. Salp.* **14** (1906-1907), 42.

Stickstoffgehalt in dem Muster.	G	T(°C)	K
13.26%	0.61	138	0.37
	0.11	123.2	0.81
	0.0057	99.5	
13.22	0.87	139.2	0.78
	0.050	117.0	0.57
	0.0048	99.5	
13.10	0.74	137.8	0.67
	0.059	118.2	0.59
	0.0054	99.5	
12.86	0.53	136.0	0.56
	0.055	118.7	0.59
	0.0048	99.5	
13.01	0.61	136.0	0.42
	0.118	123.6	0.91
	0.0054	99.5	
13.19	0.71	137.5	0.82
	0.042	117.0	0.58
	0.0041	99.5	
12.13	0.67	137.6	0.79
	0.041	117.0	0.57
	0.0041	99.5	
13.07	0.86	138.7	0.75
	0.051	116.2	0.58
	0.0052	99.3	
13.20	0.85	138.6	0.82
	0.046	116.0	0.56
	0.0048	99.0	
13.25	0.83	138.5	0.71
	0.055	117.2	0.52
	0.0060	99.5	

Eine neue Methode zur Bestimmung des Säuregehaltes des Pulvers schlägt Nic. L. Hansen[1] vor. Er begnügt sich nicht mit der Bestimmung der Nitrosäuren, sondern verfolgt das Anreichern an sämtlichen Säuren, welche durch die Zersetzung des Pulvers entstehen. Es wird nämlich die Wasserstoffionenkonzentration im Wasser, mit welchen die zuvor erhitzte Pulverprobe ausgeschüttelt wurde, gemessen. Da diese Messungen elektrometrisch, unter Anwendung von einer Chinhydronelektrode mit grosser Genauigkeit gemacht werden können, so erlaubt die Methode auch kleine Änderungen des Säuregehaltes zu verfolgen. Die Versuche wurden mit Pulverproben, welche bei 90.5°, 110° und 120° erhitzt worden sind, ausgeführt. Wenn die Versuche auf niedere Temperaturen ausgedehnt werden und somit der Temperaturkoefficient der Zerfallreaktion einwandfrei bestimmt wird, so wird man ein Mittel erhalten, um ein zuverlässiges Urteil über die Stabilität des Pulvers abzugeben. Vorläufig sind wir noch nicht so weit. Das Interesse aber welches man dieser Frage widmet, bürgt dafür, dass die Lösung des Problems nicht lange auf sich warten lassen wird.

Mandschurisches Arsenal, Mukden, China.

(1) Cit. nach L. Metz, *Z. ges. Schies- Sprengstoffw.*, **21** (1926), 186.

THE CRYSTAL STRUCTURE OF THIOUREA.

By László DEMÉNY and Isamu NITTA.

Received April 16, 1928. Published May 28, 1928.

Introduction. Now that the crystal structure of urea CON_2H_4 has been determined by Mark and Weissenberg,[1] it may be of interest to see if there is any structural relationship between the crystals of this compound and those of an analogous one, thiourea CSN_2H_4. The present investigation was made on the thiourea crystals by the Laue photographic and the X-ray spectrometric methods, of which the procedure are almost the same as already described in detail in a paper by one of the present authors.[2] Groth[3] gives the following data concerning the crystals of this compound:

> Orthorhombic bipyramidal, $a : b : c = 0.7163 : 1 : 1.1155$.
> Specific gravity, 1.406.
> Cleavage, $b\{010\}$ and $r\{101\}$ perfect.

As to the specific gravity, a value 1.450 considerably deviating from the above is also quoted as obtained in some occasion.[3] Hence another determination was made by means of a Westphal balance, which gave 1.407 in good agreement with the first-mentioned value.

The Unit of Structure. Thiourea from C.A.F. Kahlbaum was recrystallized from aqueous solution. In a case of rapid crystallization from somewhat supercooled solution, transparent six-sided plates of a few square millimetres were obtained. A Laue photograph taken with the X-rays[4] incident normally to the plate showed that this plate was parallel to the crystallographic $c(001)$ plane. In most cases of slow crystallization there grew thick prisms with rhombic bases. Several Laue photographs were obtained with a cleaved slip from the crystal, and it was found that the cleavage plane was $b(010)$. In Table 1 are given the Laue photographic data.

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(1) H. Mark and K. Weissenberg, *Z. Physik*, **16** (1923), 1.
(2) I. Nitta, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **4** (1926), No. 47, 49.
(3) P. v. Groth, "Chemische Krystallographie," 3. Teil, (1910), 555.
(4) X-rays from a Coolidge tube with tungsten anticathode.

TABLE 1. Laue Photographic Data.

hkl	$\frac{b^2}{d^2}$	$\sin\theta$	$\frac{n\lambda}{2b}$	Estim. Int.	hkl	$\frac{b^2}{d^2}$	$\sin\theta$	$\frac{n\lambda}{2b}$	Estim. Int.
(201)	8.61	0.31	0.1055	mw	(015)	21.0	0.235	0.0515	f
(211)	9.61	0.295	0.0955	w	$(01\bar{5})$	„	0.20	0.044	f
(031)	9.80	0.295	0.094	f	(214)	21.6	0.25	0.0535	mw
(221)	12.61	0.26	0.072	w	$(\bar{2}1\bar{4})$	„	0.185	0.0395	m
(231)	17.61	0.225	0.054	s	(312)	21.8	0.25	0.0535	ms
(301)	18.35	0.215	0.0505	vs	$(\bar{3}1\bar{2})$	„	0.18	0.0385	s
(141)	18.75	0.220	0.0505	s	(115)	23.0	0.235	0.0495	f
(321)	22.4	0.20	0.0425	m	$(\bar{1}1\bar{5})$	„	0.185	0.0385	f
(251)	33.6	0.17	0.029	w	(313)	25.8	0.23	0.0455	f
(341)	34.4	0.165	0.0285	w	$(\bar{3}1\bar{3})$	„	0.165	0.0325	w
(061)	36.8	0.16	0.0265	f	(215)	28.8	0.215	0.0405	m
(161)	38.8	0.16	0.0255	f	$(\bar{2}1\bar{5})$	„	0.155	0.029	ms
(512)	53.2	0.25	0.0345	f	$(\bar{3}2\bar{3})$	„	0.34	0.0635	w
(532)	61.2	0.24	0.0305	f	(314)	31.4	0.215	0.038	ms
(013)	8.20	0.365	0.1275	f	$(\bar{3}1\bar{4})$	„	0.145	0.0255	ms
$(01\bar{3})$	„	0.33	0.116	mw	(116)	31.8	0.205	0.0365	ms
(210)	8.81	0.37	0.124	w	$(\bar{1}1\bar{6})$	„	0.155	0.0275	ms
$(\bar{2}10)$	„	0.305	0.103	m	(411)	33.0	0.205	0.036	f
(211)	9.61	0.355	0.115	mw	$(\bar{4}1\bar{1})$	„	0.14	0.0245	f
$(\bar{2}1\bar{1})$	„	0.29	0.0935	m	$(\bar{3}2\bar{4})$	34.4	0.305	0.0525	w
(212)	12.01	0.325	0.0935	w	(126)	34.8	0.355	0.060	f
$(\bar{2}1\bar{2})$	„	0.255	0.0735	mw	$(\bar{1}2\bar{6})$	„	0.315	0.0535	f
(014)	13.80	0.285	0.077	w	$(\bar{4}2\bar{1})$	36.0	0.30	0.050	f
$(01\bar{4})$	„	0.25	0.0675	w	(217)	37.6	0.175	0.029	mw
(114)	15.75	0.28	0.070	mw	(315)	38.6	0.20	0.032	f
$(\bar{1}1\bar{4})$	„	0.225	0.0565	vs	(413)	39.4	0.195	0.0315	mw
(213)	16.01	0.285	0.071	mw	$(\bar{4}1\bar{3})$	„	0.125	0.020	f
$(\bar{2}1\bar{3})$	„	0.215	0.0535	s	(325)	41.6	0.345	0.0535	w
(310)	18.55	0.26	0.0605	mw	$(\bar{3}2\bar{5})$	„	0.275	0.043	mw
$(\bar{3}10)$	„	0.205	0.0475	ms					

TABLE 1 *Continued*

hkl	$\frac{b^2}{d^2}$	$\sin\theta$	$\frac{n\lambda}{2b}$	Estim. Int.	hkl	$\frac{b^2}{d_2}$	$\sin\theta$	$\frac{n\lambda}{2b}$	Estim. Int.
(423)	42.4	0.345	0.053	f	$(\bar{5}30)$	57.8	0.365	0.048	w
$(\bar{4}2\bar{3})$	„	0.275	0.042	f	(523)	60.0	0.29	0.0375	f
(027)	43.2	0.32	0.049	w	$(\bar{5}2\bar{3})$	„	0.225	0.029	f
$(02\bar{7})$	„	0.285	0.0435	mw	(327)	60.8	0.29	0.037	f
(414)	45.0	0.185	0.028	f	$(\bar{3}2\bar{7})$	„	0.225	0.029	w
(127)	45.2	0.32	0.0475	w	$(\bar{5}3\bar{2})$	61.0	0.355	0.0455	w
$(\bar{1}2\bar{7})$	„	0.275	0.0405	w	(524)	65.6	0.28	0.0345	f
(316)	47.4	0.18	0.025	w	$(\bar{5}2\bar{4})$	„	0.215	0.0265	f
(510)	49.8	0.175	0.0245	mw	(534)	70.6	0.39	0.0465	f
(227)	51.0	0.305	0.043	f	$(\bar{5}3\bar{4})$	„	0.325	0.0385	w
$(\bar{2}2\bar{7})$	„	0.25	0.035	f	(129)	70.8	0.26	0.031	f
(415)	52.2	0.175	0.0245	w	$(\bar{1}2\bar{9})$	„	0.215	0.0255	f
(512)	53.0	0.17	0.0235	w	(525)	72.8	0.265	0.031	f
(521)	53.6	0.30	0.041	f	$(\bar{5}2\bar{5})$	„	0.20	0.023	f
$(\bar{5}2\bar{1})$	„	0.24	0.033	f	(631)	80.1	0.365	0.041	w
(118)	54.2	0.16	0.022	f	$(\bar{6}3\bar{1})$	„	0.305	0.034	w
(522)	56.0	0.30	0.040	f	(536)	86.6	0.36	0.0385	f
$(\bar{5}2\bar{2})$	„	0.235	0.0315	f	$(\bar{5}3\bar{6})$	„	0.29	0.031	f
(128)	57.2	0.285	0.038	w	(721)	100.4	0.23	0.023	f
$(\bar{1}2\bar{8})$	„	0.24	0.032	w					

Note: In this Table vs, s, ms, m, mw, w and f represent very strong, strong, medium strong, medium, medium weak, weak and faint.

The dimensions of the unit cell found from the spectrometric measurements are:

$$a = 5.47,\ b = 7.64,\ \text{and}\ c = 8.54\ \text{Å.},$$

the axial ratio being thus $a:b:c = 0.716:1:1.118$. The number of chemical molecules CSN_2H_4 in the unit cell is four, and followingly the calculated density is 1.408. These values of the axial ratio and the density are in good agreement with the above-mentioned values obtained by other means than X-rays. In Table 2 are shown the results of the measurements with the ionization spectrometer.

TABLE 2.

X-ray Spectrometric Data.

hkl	Spacing		Comparative Intensities of Reflection							
	Calc.	Obs.	I	II	III	IV	V	VI	VII	VIII
(100)	5.48	5.48	0 (0)	60 (55)	0 (0)	7 (8.6)	0 (0)	0 (2.1)	0 (0)	0 (2.9)
(010)	7.65	7.64	0 (0)	200 (274)	0 (0)	0 (2.3)	0 (0)	5.2 (5.4)	0 (0)	2 (3.2)
(001)	8.54	8.54	0 (0)	220 (280)	0 (0)	22 (29)	0 (0)	31 (36)	0 (0)	13 (18)
(021)	3.49	3.48	80 (90)	16 (22)						
(011)	5.70	5.70	0 (0)	80 (89)	0 (0)	16 (18)				
(012)	3.73	3.73	0 (0)	40 (24)						
(201)	2.61	2.61	0 (0)	16 (13)						
(101)	4.61	4.60	45 (83)	9 (14)	13 (14)	20 (11)				
(102)	3.37	3.37	0 (0)	18 (19)						
(210)	2.58	2.58	0 (0.9)	10 (9)	1 (4)					
(110)	4.45	4.46	170 (183)	0 (3.3)	0 (2.7)	10 (8.5)				
(120)	3.14	3.13	210 (141)	15 (21)	3 (7)					

The Space Group. On inspecting the data in Tables 1 and 2, various reflecting planes were found to show the following characteristics:

(1) In the first order reflection from pyramidal planes, there are all kinds of combinations of even and odd integers for their indices h, k and l.

(2) No odd order reflection is observed from any of the planes (100), (010) and (001).

(3) All prismatic planes are divided into two groups, (A) and (B):

(A) The prismatic planes, having the indices of (zero, even, odd), (odd, zero, odd), (odd, odd, zero), (odd, even, zero) or (even, odd, zero), show odd order reflections; e. g. (021), (061), (027), (101), (301), (110), (310), (510), (120), (210).

(B) Those, having the indices of (zero, odd, odd), (zero, odd, even), (even, zero, odd) or (odd, zero, even), show no odd order reflection; e. g. (011), (012), (201), (102).

From (1) it is obvious that the corresponding space group should be one of those that are based upon the simple orthorhombic translation group

Γ_0; viz. one of the space groups C_{2v}^1 to C_{2v}^{10}, V^1 to V^4, and V_h^1 to V_h^{16}.[1] While, in the general criteria of the space groups, the conditions for the presence of certain reflection may not fully correspond to the experimental data, all the requirements for the absence should be necessarily satisfied, or, in the present case, any space group that is in conflict with the evidence (3A) can never be chosen as the corresponding one. Accordingly (3A) was first used to sort out the possible space groups, and these were found to be C_{2v}^1, C_{2v}^2, C_{2v}^4, C_{2v}^7, C_{2v}^9, V^1, V^2, V^3, V^4, V_h^1, V_h^5, V_h^{13} and V_h^{16}. Of these space groups C_{2v}^9 and V_h^{16} are fitted exactly to all the conditions (1) to (3), whereas the rest may show odd order reflections from more sorts of planes than those in (3A). As already noticed, it may also be possible for any of the above space groups other than C_{2v}^9 and V_h^{16} to account for the observed nonpresence of the predicted reflections, but, to do this, atoms should be arranged at some special positions. In the present case, however, this is very improbable, if not impossible, and it seems unnecessary to treat such space groups further. As to C_{2v}^9 and V_h^{16}, it is impossible so far to distinguish one from the other, the general criteria coming to the same.[2]

The Atomic Arrangement. In case that the corresponding space group is C_{2v}^9,[3] the crystals of thiourea must have hemimorphic polarity along the *c*-axis, whose existence, however, has never been proved. On the other hand, since the space group V_h^{16} is in accord with the observed symmetry, it may be regarded as the correct one, if there is found an arrangement of atoms which accounts for the observed data respecting the comparative intensities of reflection. The space group V_h^{16} has the following equivalent positions[4] in all:

Four-fold positions

(a) $0\ \frac{1}{4}\ \frac{1}{4}$; $0\ \frac{1}{4}\ \frac{3}{4}$; $\frac{1}{4}\ \frac{3}{4}\ \frac{3}{4}$; $\frac{1}{2}\ \frac{3}{4}\ \frac{1}{4}$.

(b) $\frac{1}{2}\ \frac{1}{4}\ \frac{1}{4}$; $\frac{1}{2}\ \frac{1}{4}\ \frac{3}{4}$; $0\ \frac{3}{4}\ \frac{3}{4}$; $0\ \frac{3}{4}\ \frac{1}{4}$.

(c) $u\ v\ 0$; $-u, \frac{1}{2}-v, \frac{1}{2}$; $\frac{1}{2}-u, \frac{1}{2}+v, 0$; $\frac{1}{2}+u, -v, \frac{1}{2}$.

(1) See for instance R.W.G. Wyckoff, *Am. J. Sci.* **9** (1925), 145, or H. Mark, "Die Verwendung der Röntgenstrahlen in Chemie und Technik," (1926), 387.

(2) Very recently Professor S. Nishikawa and Mr. K. Matukawa (*Proc. Imp. Acad. (Japan)*, **4** (1928), March) have found an effect of hemihedry of zincblende upon X-ray reflection, but it it not yet applicable to the present case.

(3) As the general equivalent positions are four-fold here and the unit cell contains four chemical molecules CSN_2H_4, it can be inferred that the shape of the molecule is not restricted by any condition of symmetry, the parameters to be determined being more than ten.

(4) See for instance R.W.G. Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," (1922), or H. Mark, loc. cit., Table 52.

Eight-fold positions

(d) $x\,y\,z$; $-x, \frac{1}{2}-y, \frac{1}{2}+z$; $\frac{1}{2}-x, \frac{1}{2}+y, -z$; $\frac{1}{2}+x, -y, \frac{1}{2}-z$;

$-x, \frac{1}{2}-y, \frac{1}{2}-z$; $x, y, -z$; $\frac{1}{2}+x, -y, \frac{1}{2}+z$; $\frac{1}{2}-x, \frac{1}{2}+y, z$.

The positions (a) and (b) coincide with the centres of symmetry, and (c) are in the planes of symmetry. There are four molecules in the unit cell, so that four atoms of carbon, four atoms of sulphur, eight atoms of nitrogen and sixteen atoms of hydrogen should be arranged in it. As is generally the case for organic crystals, it is highly probable that the crystals of thiourea will form a molecular lattice. If so, the 4C atoms or the 4S atoms cannot be placed in the positions (a) or (b); for no atomic arrangement can give a centre of symmetry to a single molecule CSN_2H_4. The observed comparative intensities of reflection from principal planes also favour to exclude such possibilities. Accordingly the atoms of carbon and sulphur should be arranged in the planes of symmetry, their positions being (c) with respective set of parameter values. That the nitrogen atoms should be arranged in the general equivalent positions (d) comes out directly from the inspection of the distribution of intensities of reflection among various orders from (001) plane. Sixteen hydrogen atoms will be divided into two groups, each being situated at (d).

In determining the arrangement, the atoms of hydrogen may be neglected as usually done, then there is only one parameter z_N for the nitrogen atoms in the direction of the c-axis. A value about 0.144 for z_N was found to account well for the observed distribution of the intensities of reflection among various orders from (001). With this value the distance between the two nitrogen atoms in a molecule becomes about 2.46 Å. As this seemed not in the least inadequate, it was further attempted to determine the values of the remaining parameters, which, being as many as six, will hardly be evaluated without some assumption. Therefore, it was assumed that one carbon atom and two nitrogen atoms form an isosceles triangle NCN (Fig. 1), the distance between the two N atoms being the above value 2.46Å., and that between the carbon atom and one of the nitrogen atoms being very nearly 1.44—1.48 Å. as found in the case of hexamethylene tetramine.[1] Upon this a trial survey was made, and it was

(1) R.G. Dickinsonand A.L. Ra ymond, *J. Am. Chem. Soc.*, **45** (1923), 22; H.W. Gonell and H. Mark, *Z. physik. Chem.*, **107** (1923), 181.

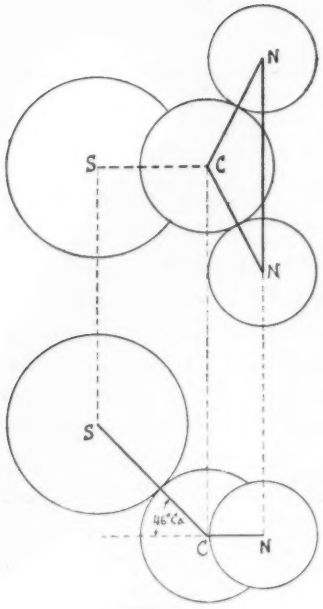

Fig. 1.

Discussion of the Structure. With the above parameter values the C, S and 2N atoms in a molecule do not lie in the same plane, but the direction from the carbon to the sulphur atom makes an angle of about 46° to the plane NCN. The interatomic distance between sulphur and carbon is 1.81Å., which is in good agreement with the sum of radii of the neutral atoms for S and C, $1.04+0.77=1.81$Å. according to Wyckoff[1] or Goldschmidt.[2] Each one of the found that a set of parameter values accounted for the comparative intensities given in Table 2. These values are: $u_C = 0.186$, $v_c = 0.144$ for the carbon atoms; $u_S = -0.095$, $v_S = 0.270$ for the sulphur atoms; and $x_N = 0.300$, $y_N = 0.164$, $z_N = 0.144$ for the nitrogen atoms. In Table 2, the figures without brackets are the intensities observed and those within brackets right under them are the intensities calculated by a formula $\left(\frac{d}{n}\right)^{2.35} |S|$, where d denotes the spacing, n the order of reflection and $|S|$ the absolute value of structure amplitude, the reflecting powers of the atoms being roughly assumed to be proportional to their atomic numbers.

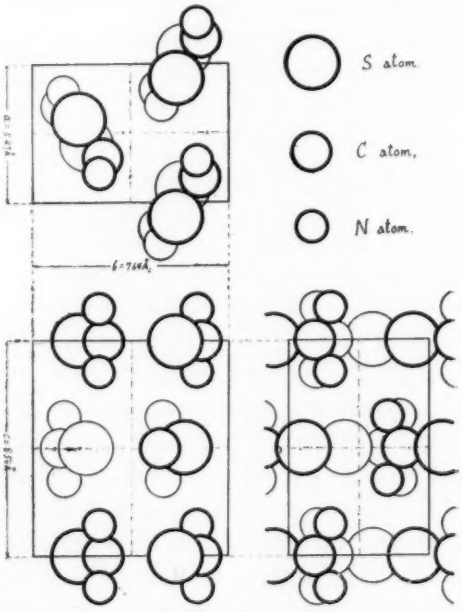

Fig. 2.

(1) R.W.G. Wyckoff, *Proc. Nat. Acad. Sci.*, 9 (1923), 33.
(2) V.M. Goldschmidt, *Skrifter Norske Videnskaps-Akad. Oslo. I. Matemat.-Natur. Klasse*, (1926), No. 2.

nitrogen atoms is at a distance of 1.39 Å. from the carbon atom, which is somewhat less than the value in hexamethylene tetramine or the sum of radii of the neutral carbon and nitrogen atoms 0.77 + 0.71 = 1.48A. according to Goldschmidt, but is concordant with the sum 0.77 + 0.63 = 1.40 Å. given by Wyckoff. To complete the crystal structure of thiourea, the positions of the hydrogen atoms hitherto neglected should be considered, and, as a matter of fact, there is a vacant place left for them to be so arranged that the molecular structure may correspond to the usual chemical formula $SC(NH_2)_2$. As for the connection between neighbouring molecules, it is closer in the *zx*-plane than in the direction of the *y*-axis, which corresponds to the existence of perfect cleavage on (010) plane. Besides, it may also be noted that the largest spacing was found in the direction of the *c*-axis to be $d_{(001)} = 8.54$ Å., and, as already described, there was actually observed a case in which thiourea crystallized in plates parallel to (001)[1]. The arrangement of atoms in the crystal is shown in Fig. 2.

According to Hark and Weissenberg, urea crystallizes in the space group V_d^3 of the tetragonal scalenohedral class, the unit cell being of the dimensions $a = 5.63$ and $c = 4.70$ Å. The molecule is tied up spatially in one group, is flat on neglection of H atoms and has the proper symmetry of C_2^v. Such a structure of urea seemingly bears no close relation to that of thiourea. This may correspond to the separate crystallization from the aqueous solution containing these compounds. The unit cell of the former contains two chemical molecules CON_2H_4, and the line joining the two nitrogen atoms of a molecule stands perpendicular to that of the other, while the unit cell of the latter contains four molecules CSN_2H_4, and the corresponding lines for every pair of nitrogen atoms are all parallel to each other. The distance between the two N atoms in the molecule is about 2 Å. for urea, and 2.46 Å. for thiourea. As to the molecular symmetry, C_s of the latter is lower than C_2^v of the former. In spite of these differences, however, they are not quite unrelated to each other; for it is also possible to change the crystal structure of thiourea into that of urea by making every molecule flat in the *zx*-plane and giving it a small amount of translation and a rotation through half a right angle about the axis C–S.

In conclusion, the authors wish to express tl ir best thanks to Professor S. Nishikawa for his kind interest and encouragement during the work.

(1) cf. H. Mark, loc. cit., 340.

Summary.

Using the Laue photographic and X-ray spectrometric methods the crystal structure of thiourea was investigated. The unit of structure built upon the simple orthorhombic translation group Γ_0, is of the dimensions $a = 5.47$, $b = 7.64$ and $c = 8.54$ A., and contains four chemical molecules of CSN_2H_4. Thus the density is 1.408. The plausible space group being V_h^{16}, a possible atomic arrangement, neglecting H atoms, was found to be as follows:

$$4C\left\{u, v, 0;\quad -u, \tfrac{1}{2}-v, \tfrac{1}{2};\quad \tfrac{1}{2}-u, \tfrac{1}{2}+v, 0;\quad \tfrac{1}{2}+u, -v, \tfrac{1}{2}\right\}$$

with $u = 0.186$, $v = 0.144$;

$$4S\left\{u, v, 0;\quad -u, \tfrac{1}{2}-v, \tfrac{1}{2};\quad \tfrac{1}{2}-u, \tfrac{1}{2}+v, 0;\quad \tfrac{1}{2}+u, -v, \tfrac{1}{2}\right\}$$

with $u = -0.095$, $v = 0.270$; and

$$8N\left\{\begin{matrix} x, y, z;\quad -x, \tfrac{1}{2}-y, \tfrac{1}{2}+z;\quad \tfrac{1}{2}-x, \tfrac{1}{2}+y, -z;\quad \tfrac{1}{2}+x, -y, \tfrac{1}{2}-z; \\ -x, \tfrac{1}{2}-y, \tfrac{1}{2}-z;\quad x, y, -z;\quad \tfrac{1}{2}+x, -y, \tfrac{1}{2}+z;\quad \tfrac{1}{2}-x, \tfrac{1}{2}+y, z \end{matrix}\right\}$$

with $x = 0.300$, $y = 0.164$ and $z = 0.144$. The molecule has the symmetry of C_s, i.e. it has one plane of symmetry in it. In such a model, the distance C–S is 1.81 Å., and that C–N is 1.39 Å. Discussion was also made upon its crystalline and molecular structures in comparison with those of urea.

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